

(APPENDIX 1)

Potential for Asphaltenic Bottom Cracking Technology
in Upgrading Ultra-Heavy Oil

by

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1. Introduction

The need for residuum conversion by refineries is indicated by two trends visible in long-range forecasts. One is a gradual rise in demand for transportation fuels, and the other is a fall in consumption of heavy fuel oil. Weakening demand for heavy fuel oil is resulting from energy conservation in industry, changes in the industrial structure, and substitution by alternative fuels such as coal, natural gas and nuclear power. Moreover, the trend in available crude oil supplies is toward heavier crudes.

In Japan, refineries have responded by installing residue conversion equipment (vacuum residue desulfurizer and visbreaker) and modifying existing residue hydrodesulfurization (HDS) units to high-conversion types. Also, FCC units have been installed or modified to treat feedstocks containing residue. Modification of existing residue HDS units involved the addition of reactors that operate at higher temperature with the aid of newly developed hydrodemetallation catalyst or asphaltenic bottom cracking (ABC) catalyst. ABC catalyst was adopted because of its demonstrated capability to process bottoms of heavier crudes that contain higher metals and asphaltenes, along with its longer service life and higher distillates yield in higher-temperature operation.

The need for an economical method of achieving greater residue conversion has led us to develop the VisABC process, a combination of thermal conversion with ABC catalytic conversion. We expected that overall conversion of residue would be enhanced by following thermal conversion of the residue by catalytic conversion of the asphaltenes produced and that degradation of product quality would be prevented by hydrogenation with ABC catalyst. Experimental results with Arabian Heavy vacuum residue proved that 60% residue conversion can be obtained with favorable product quality and no sludge formation, and that catalyst life can be maintained for about 8,000 hours.

The VisABC process fully utilizes low-cost thermal reaction to achieve maximum residue conversion in a fixed catalyst bed. In this paper, test results are discussed and the economic advantage of the VisABC process is shown by a refinery study in which Arabian Heavy and Orinoco (Cello Negro) heavy crudes were processed.

2. Commercial Experience with ABC Catalyst (Saito et al., 1984)

Okinawa Sekiyu Seisei Co., Ltd. attempted to treat heavy feedstocks such as 427°C⁺ fractions of Arabian and Iranian heavy crude oils and heavy residues transferred from other parts of Japan, converting them to middle distillate by higher-temperature operation. The company has obtained good results by replacing part of

the HDS catalyst in its residue HDS unit with ABC catalyst. The company's refinery is basically a hydroskimming-type refinery. The heart of its configuration is a complex of atmospheric crude unit and residue HDS unit that plays the key role in treating heavy crude residues.

ABC catalyst shows extremely high resistance to deactivation by deposited carbon and metals. Such deactivation is generally a serious problem with conventional HDS catalyst when residues of heavy crude oils are processed. For example, the activity of ABC catalyst declines very slowly until metal deposition reaches about 70 wt% on fresh catalyst -- a sharp contrast with conventional HDS catalyst, which loses its activity almost completely at about 30 wt% average metal deposition (Takeuchi, 1983). However, since ABC catalysts has lower activity for the hydrodesulfurization reaction than does HDS catalyst, it was combined with HDS catalyst to meet the requirement of sulfur level in product oils.

In this case, ABC catalyst was loaded in the upper part of the reactor bed, comprising 33 vol% of the total volume. Feedstock to the HDS unit was a mixture of 427°C+ fractions of Arabian Heavy, Iranian Heavy, Arabian Medium and Isthmus blend. Table 1 shows typical feed and product yields and properties at 43% of 538°C+ conversion.

The metal level in the first bed of ABC catalyst was found to be in the range of 41 to 55 wt% by analysis of the spent catalyst. In spite of this relatively high metal deposition, the pressure drop across the reactor did not increase throughout the operation. Moreover, both ABC and HDS catalysts were removed from the reactors without trouble at the end of the operation, proving that high metal deposition on ABC catalyst had no direct correlation with catalyst-bed plugging.

To date, about 400 metric tons of ABC catalyst has been charged to existing residue HDS units, confirming the catalyst's performance as estimated from laboratory tests for various feedstocks.

3. VisABC Process

3.1 Reaction (Nakata et al., 1984)

Since residue conversion is achieved economically by thermal conversion, the VisABC process, which combines visbreaking and ABC catalytic conversion, was proposed and tested on a pilot plant ~~scale~~. It was expected that overall residue conversion would be enhanced by visbreaking, while ABC catalyst would crack the condensed aromatic materials produced by visbreaking to lighter

fractions and would maintain favorable product quality even at high conversion. Tests were made of visbreaking (VB) and of two combinations: hydrovisbreaking with ABC (HVB/ABC) and visbreaking with ABC (VB/ABC). These two combinations are the two versions of the VisABC process. Product yields and properties resulting from the test runs with Arabian Heavy VR are listed in Table 2, along with the feedstock properties.

As shown in the Table, VB causes an appreciable increase in asphaltenes and CCR. By contrast, VB/ABC results in sharp decreases in asphaltenes and CCR, and to lower levels of sulfur, metals and viscosity as well. Still further reductions are seen with HVB/ABC.

To investigate the respective changes in constituents in residual oil processed respectively by VB, VB/ABC and HVB/ABC, tests were undertaken using Kafji (KF) VR as feedstock with test schemes and conditions as shown in Figure 1. The product oils were separated into asphaltenes (n-heptane insolubles) and maltenes (n-heptane solubles) by extraction. The asphaltenes were further separated into three subfractions by elution volume, using gel permeation chromatography. The maltenes were also further separated into four hydrocarbon type, namely, saturates, aromatics-I, aromatics-II and polar aromatics, using centrifugal liquid chromatography. The distribution of maltenes and asphaltenes and of their subfractions is shown in Figure 2 for feedstock KF VR and for oils produced by VB, VB/ABC and HVB/ABC. Further, average chemical structure of both maltenes and asphaltenes subfractions are analyzed mainly by ^1H and ^{13}C -NMR as shown in Figure 3 and Figure 4 respectively in which chemical structures of maltenes subfractions of VB, VB/ABC and HVB/ABC are almost the same while those of asphaltenes vary in accordance with the treatment.

From the figures, it is seen that visbreaking considerably increased the yield of asphaltenes. At the same time, yield of aromatics and polar aromatics, which are regarded as peptizing materials for asphaltenes, is decreased. This destabilizes the asphaltenes and precipitates them at high residue conversion. Further treatment of this visbroken oil by ABC catalyst under hydrogen pressure results in greater yield of peptizing materials, lower yield of asphaltenes and smaller numbers of unit structures in asphaltenes. These changes strongly stabilize asphaltenes and allow higher residue conversion in spite of the detrimental effects of increased saturate yield and enlargement of unit structure in asphaltenes.

With HVB/ABC, still lower asphaltenes yield and reduced numbers of unit structures in asphaltenes can be seen. This makes asphaltenes more stable in solution. The most severe residue conversion can be expected with the HVB/ABC process, and this is confirmed by other pilot tests. Further conversion, however, seems difficult, because higher yield of saturate together with lower yield of

peptizing materials is thought to weaken the ability of product oil to keep asphaltenes in solution, in spite of the low yield of asphaltenes.

The change of asphaltene content with severity of operation (538°C^{+} conversion) were investigated for processing respectively by VB, HVB and HVB/ABC. The results are shown in Figure 5. Asphaltenes content rises with increasing conversion for VB, and also rises -- but less rapidly -- for HVB. It is remarkably reduced, however, by hydrotreating with ABC catalyst.

Tests were also made to clarify the maximum residue conversion attainable with VB, residue HDS and VisABC processes respectively, using Arabian Heavy VR. Maximum conversion is determined by a limit beyond which condensed carbonaceous materials (dry sludge*) begin to precipitate in the product oil. Conversion beyond this limit is undesirable because the formation of dry sludge not only degrades product quality but also causes fouling and finally plugging of downstream lines and equipment. Figure 6 shows the relationship between extent of conversion and tendency toward dry sludge formation as represented by compatibility (xylene equivalent). The dotted lines represent the boundary of xylene equivalent beyond which dry sludge is observed in the product oils. For Arabian Heavy VR, the maximum conversions are found to be around 60 wt% for VisABC, 45 wt% for residue HDS and 30 wt% for VB.

3.2 Typical Yield and Properties

Table 3 shows properties of Arabian Heavy and Orinoco (Cello Negro) VR and estimated product yields and properties, based on the VisABC pilot-plant tests. Conversion is set at 60 wt%, which is the maximum value for Arabian Heavy, for both feedstocks. Continuous pilot plant operation for one year, treating a Arabian Heavy vacuum residue, has shown that metals deposited and accumulated on ABC catalysts as expected and influenced the catalyst activity as predicted. Orinoco VR as well as other Venezuelan VRs were tested for about half a year in our pilot-plant (Takeuchi et al, 1982). Based on experience with both pilot-plant and commercial-plant operations, catalyst life is concluded to be half a year when Orinoco VR is treated.

3.3 Process

Figure 7 is a schematic diagram of the VisABC process. Residual feedstock from atmospheric and/or vacuum distillation is charged to the unit by a high-pressure pump and is mixed with hydrogen-rich gas. The feedstock combined with hydrogen is heated in heat exchangers and thermally cracked to a predetermined degree of conversion in the hydrovisbreaking heater by control of the temperature profile throughout the heater coil. The cracked oil is

* measured by hot-filtration method with n-heptane as washing material

immediately quenched at the heater exit with hydrogen-rich gas to prevent undesirable effects due to excessive cracking. The quenched cracked oil passes through the guard reactor and is then routed to the fixed-bed reactors for secondary cracking. In these reactors, asphaltene that is latent in the original feedstock and is formed in the visbreaking section is effectively hydrocracked with the aid of ABC catalyst to achieve further conversion and to improve the product quality. The ABC reactor's inlet temperature is controlled by injection of hot, recycled hydrogen. If further desulfurization is required, an appropriate HDS catalyst is loaded after the ABC catalyst. The effluent from the reactors is sent to a series of hot and cold flash drums for hydrogen recovery and recycle. The flashed gas and vapor are sent to the purifier to remove hydrogen sulfide. The flashed effluent is sent to the fractionator and separated into desired cuts of product.

4. Economics of VisABC

For an economic evaluation of the VisABC process for upgrading heavy oils, we have chosen as the basis a 100,000 BPCD grassroots refinery with self-sufficient utilities supply, processing Arabian Heavy crude or Orinoco heavy oil to produce the same product mix, including international marketing grades of motor gasoline, middle distillate and low-sulfur fuel oil. Table 4 summarizes the study basis and Table 5 shows the properties of the crudes.

Special features of Orinoco heavy oil are its very high yield of 482°C+ fraction (61.8 vol%) and its high metals content (532 ppm), which seem to be key points in its processing economics. Figure 8 shows the refinery block flow diagram, indicating optimized flow rates for Orinoco heavy oil. Crude oil is processed by atmospheric distillation and vacuum flashing to produce distillates and vacuum residue. The latter is charged to the VisABC unit, where 60 wt% of residue is converted to lighter fractions. VR fraction from the VisABC unit is utilized as fuel oil blend. Distillates from the unit are blended with corresponding distillates from atmospheric distillation accordingly. A relatively large hydrocracker is needed for middle-distillates production to compensate for the aromatic nature of Orinoco heavy oil.

Table 6 summarizes the product yields and major product specifications used in the study. Total marketable products amount to 100.2 vol% and 98.4 vol% of feed for Orinoco and Arabian Heavy crudes respectively, due to volume expansion by conversion processes such as hydrocracking, VisABC and FCC. On the other hand, the yields of No.6 fuel oil reflect the yield of residue in the feedstocks.

Table 7 summarizes investment costs and refining costs for the cases of Arabian Heavy crude and Orinoco heavy oil. The differences in capacity of cracking units and investment cost between Orinoco and Arabian Heavy crudes result from the high yield of both VGO and VR fractions in Orinoco heavy oil. The refining cost of Orinoco is \$8.90/bbl of crude, compared to \$6.00/bbl of crude for Arabian Heavy while the yields of No.6 fuel oil are minimized to 21.3 vol% and 4.9 vol% of crudes for Orinoco and Arabian Heavy crudes respectively by VisABC unit. The refining cost difference between the two crudes comes from the difference in capital recovery cost and the cost of catalyst and chemicals, which can be attributed to the high residue yield and high metals content of Orinoco heavy oil.

For further evaluation of refining cost of the both crudes, a study was made assuming the same product slates. The results are shown in Figure 9. It can be seen from the figure that refining cost difference of Orinoco over Arabian Heavy crudes falls into the range of \$4.30/bbl to \$4.60/bbl of crudes for the same production of No.6 fuel oil.

5. Conclusion

Extensive commercial experience has been obtained in the use of ABC catalyst for processing high-metal and high-asphaltene residues in residue HDS units in Japan. Sufficient experience in test-processing of Orinoco residue has also been gained.

The VisABC process, based on the excellent performance of ABC catalyst in high-temperature operation, is expected to provide the maximum attainable residue conversion of heavy residues in a fixed catalyst bed with favorable product quality. Changes in content of both maltenes and asphaltenes explain how high conversion is achieved by the VisABC process.

An economic study of refineries processing 100,000 BPCD of Orinoco or Arabian Heavy crude shows that Orinoco can be upgraded at a processing cost about \$4.30/bbl to \$4.60/bbl of crude higher than that of Arabian Heavy on the same products slate basis.

From these facts, it is firmly believed that the application of the VisABC process to the upgrading of residues, including Orinoco, will gain practical importance in the near future.

Literatures Cited

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